# Aerosol Measurements at Cheju Island During ACE-Asia: Aerosol Number Size Distributions, Particle Hygroscopicity, and Individual Particle Size and Chemical Composition

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## I. INTRODUCTION

The upcoming Aerosol Characterization Experiment (ACE-Asia) represents an effort to measure ambient aerosol properties in a vast region that is characterized by an extremely complex mixture of aerosol sources. Aerosol size distribution and chemical composition measurements, coupled with measurements of relevant trace-gas species at many locations will be required to successfully capture the variability inherent in urban and regional scale transport patterns and rapid gas/particle partitioning. Size and chemical composition, are very fundamental properties of atmospheric aerosols. Without an improved understanding of these properties, significant progress in the evaluation of aerosol radiative effects cannot be made. The inherent heterogeneity of the aerosol system, (more so in the Asian outflow region), requires a detailed knowledge of size dependent chemical composition. To test process-oriented models driven by emission inventories, meteorology, and chemistry, it is critical to be able to distinguish between internally and externally mixed aerosols. Only through single-particle chemical composition analysis can this type of information be obtained.

Many atmospheric aerosols contain hygroscopic material. At increased relative humidity (RH), these particles grow in size and more effectively scatter radiation. Consequently, the radiative impact of aerosols is strongly RH dependent. In-situ measurements of size-dependent hygroscopicity provide extremely valuable information for understanding the influence of particle hygroscopicity on direct and indirect radiative forcing. The lifetime of atmospheric aerosols, and therefore their radiative impact, is also a function of their hygroscopicity and ambient RH. Gas-to-particle conversion of water-soluble species on non-hygroscopic carbonaceous and dust particles can render them more hygroscopic. Models must accurately simulate these processes, so that a realistic picture of the radiative impacts of Asian aerosols and the processes that control them can be painted.

To address the need for intensive aerosol physical and chemical characterization techniques, the Environmental Chemistry Division at Brookhaven National Laboratory has developed a novel, state-of-the-art measurement system. This system is capable of providing in-situ, real-time rapid measurements of particle size distributions from 3nm to 1 micrometer by mobility analysis. A Forward Scattering Spectrometer Probe (FSSP-100) is used to measure size distributions between .3 to 50 micrometers at ambient conditions. Size and chemical composition of individual-particles, over the 20nm to 10 micrometer size range is measured by Time-of-Flight Mass-Spectrometry (TOF-MS). In parallel, measurements of size-resolved hygroscopicity, volatility and particle surface characteristics, can be obtained through the use of a Tandem Differential Mobility Analyzer (TDMA) system. Single-particle information from the TOF-MS can be placed into context with respect to size-resolved physical and thermodynamic properties through the combined use of TDMA and the ambient number size distribution.

We propose to conduct intensive measurements of aerosol size, concentration, hygroscopicity and chemical composition at Cheju Island, Korea (126$^{o}$10' E, 33$^{o}$17' N), during the ACE-Asia intensive operating period. Cheju Island is an ideal sampling site. It is uninfluenced by local anthropogenic particle sources and is ideally located to enable the study of air masses that have been influenced by Korea, China and Japan during one-to-seven day transport times over the Yellow Sea. These measurements would provide critical information with which to validate model calculations of aerosol size and chemical evolution along air mass trajectories

originating over eastern China, which is an important source of anthropogenic pollutants to the Pacific Ocean.

## II. BACKGROUND

Previous studies (Hayami and Carmichael, 1998; Carmichael et al., 1996; Kim et al., 1998a; Chen et al., 1997) have found significant changes in aerosol loading at Cheju Island that were associated with changes in air mass back-trajectories, particularly when the Gobi desert in China was the dominant source region. Other studies have examined bulk aerosol composition, and found that particulate nitrate peaked coincidentally with high concentrations of non-sea salt calcium. These findings suggest that desert dust particles are an important sink for gas-phase nitrate. Our measurements will provide detailed information on the size-resolved composition on a particle-by-particle basis and will allow the role of desert dust in these processes to be assessed accurately.

Studies of bulk composition of ambient aerosols at Cheju Island have found a strong dependence on meteorological conditions. Periods with air mass trajectories passing over heavily populated regions of South Korea, China, and Japan were associated with higher levels of organic carbon, elemental carbon and particulate nitrate (Kim et al., 1998b). Bulk composition results, however, cannot provide information on the size-resolved properties, or on the internal versus external mixing state of the various species present in the ambient aerosol. Hayami and Carmichael (1998) point out that the desert dust input from China to the Yellow Sea region represented a significant perturbation to the regional radiative forcing by ambient particles. The ambient aerosol radiative properties will depend upon the mixing state and the distribution of chemical species with particle size. Our individual particle composition and number size distribution results will allow the first quantitative estimates to be made of the size-resolved mixing state of ambient particles in this region.

Arimoto et al. (1996) studied the concentrations of particulate sulfate, nitrate, methanesulfonic acid (MSA) and trace metals at Cheju Island and other locations in the North Pacific. They found that non-sea-salt sulfate (nss-$SO_4$) was not well correlated with MSA at Cheju, suggesting that anthropogenic, and not biogenic, sources of sulfate controlled nss-$SO_4$ concentrations at the island. The importance of anthropogenic sources of particulate matter at Cheju was also indicated by the correlation between nss-$SO_4$ and particulate nitrate as found by Arimoto et al. (1996). In this study, measurements of trace metals and nitrate at Hawaii and other remote Pacific islands were used to demonstrate that long-range transport of dust to the North Pacific from East Asia was accompanied by the transport of anthropogenic material. Measurements of the size, concentration, and individual particle composition at Cheju are designed to provide important information for models that attempt to simulate the radiative forcing of dust, transported over remote regions of the North Pacific. Furthermore, our measurement results will serve as important inputs to hill cap cloud studies that will be conducted by other ACE-Asia investigators at Cheju. To determine the extent to which the dust composition has been anthropogenically perturbed, our studies will search for and detect species like nitrate and sulfate within individual dust particles.

## III. EXPERIMENTAL APPROACH

### a. Individual Particle Size and Chemical Composition

Recent advances in single particle mass spectroscopy have made possible real-time characterization of size and chemical composition of individual particles on (Carson et. al., 1995; Murphy et al., 1995; Gardet al., 1997). Figure 1 shows single particle mass spectra of three particles observed at site in Colorado (Murphy et al., 1997a). It shows that all three particles are somewhat internally mixed, and also that the particles are very different from each other. This simple figure provides a vivid illustration of the heterogeneity and complexity of atmospheric

aerosols. No other in-situ measurement technique has the capacity to generate composition information with a similar level of detail.

Tang 1997 presents a comparative study of the effect of internal vs. external mixing on light scattering by aerosols. He has shown that as long as the relative humidity remains above the efflorescence point, the light scattering coefficients of internally and externally mixed aerosols composed of hygroscopic salts differ only by 10 to 20%. However, at relative humidities below efflorescence the differences can be very significant. Studies in our laboratory on internally mixed hygroscopic aerosols containing insoluble components such as $CaCO_3$ show a significant change in the efflorescence point at RH slightly below 50%.

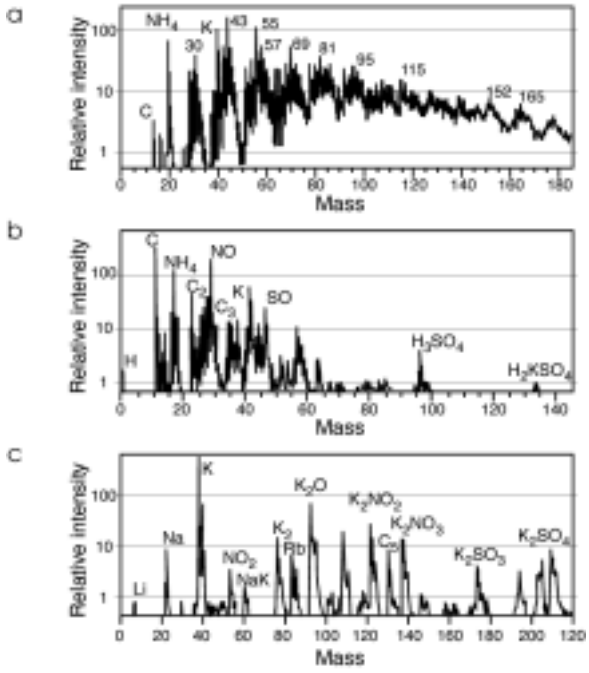



**Figure 1.** Positive-ion mass-spectra of three particles, recorded at Idaho Hill during the month of September 1995. Note the substantial particle-to-particle variations in composition. Particle a. is largely organic, with small contribution from inorganic ions. Particle b. exhibits a mixed composition organic and inorganic. Particle c. consists primarily of inorganic species including nitrates, sulfates, and a large variety of counter ions (after Murphy and Thomson, 1997a).

Detailed size and composition information at the individual particle level provides critical input to radiative closure studies. Clearly, models cannot ***quantitatively*** reproduce the radiative effects of aerosols unless they represent the aerosols in their appropriate mixing state. While the contribution of single particle spectroscopy to quantitative studies is important, the knowledge of each individual particle's internal vs. external mixing-state provides ***qualitative*** insight that has far more important implications. The composition of each particle carries with it a story of the ***aerosol life cycle*** from birth to the point of observation. The competition for condensable oxidation products between new particle formation by homogeneous nucleation and particle growth is constantly occuring. For example, when a dust particle from the Gobi desert is transported to Cheju Island, it undergoes physical and chemical processing. This processing alters the particles, resulting in deposits of sulfate, nitrate, and organic species and creating internally mixed particles. In contrast, if the surface area of preexisting particles is low, new particles may instead be formed by homogeneous nucleation. These freshly produced particles would appear to be chemically purer.

The ultimate goal of this research is to help develop reliable process driven models that combine emission inventories of primary particles and particle precursors with climatologic inputs to simulate atmospheric aerosols. The calculated aerosol fields serve as inputs to radiation models. It is only through the comparison between simulated and observed particle compositions and size distributions that the correct representation of the aerosol life cycle, including formation, growth, and deposition, in the models can be tested. Comparisons between data and

simulation of the degree of internal mixing provide immediate feedback on the representation of the aerosol life cycle. In particular:

- ***Single particle mass spectra provide critical information for quantitative closure studies.***
- ***Single particle mass spectra provide critical information for qualitative tests of process driven simulations.***

Several versions of single particle mass spectrometers have been deployed in atmospheric studies (Murphy et. al., 1999; Murphy and Thomson, 1997a; 1997b; Noble and Prather, 1996; 1997; A. Wexler, private communication). These pioneering studies have already had an important impact in shaping our view of the nature of atmospheric aerosols. Each instrument brings with it some unique features, and constant development and upgrades are producing new capabilities.

The BNL Single Particle Laser Ablation Time of Flight Mass Spectrometer (SPLAT-MS; Fig. 2) is designed to be a universal tool for characterizing the size and composition of individual aerosols from 20 nm up to a few micrometers. It uses whole particle time of flight for size determination and laser ablation synchronized with the particle's arrival at the inlet to the TOF-MS to evaporate and ionize the components for time of flight mass spectroscopic analysis. The instrument is designed to operate in two different detection modes, photoionization for small (<100nm) particles and light scattering for large (>100nm) particles. Since the switch between the two modes is electronic and does not require any hardware modification it can be automated to respond to the streaming aerosol size distribution data simultaneously measured using electrical mobility techniques.

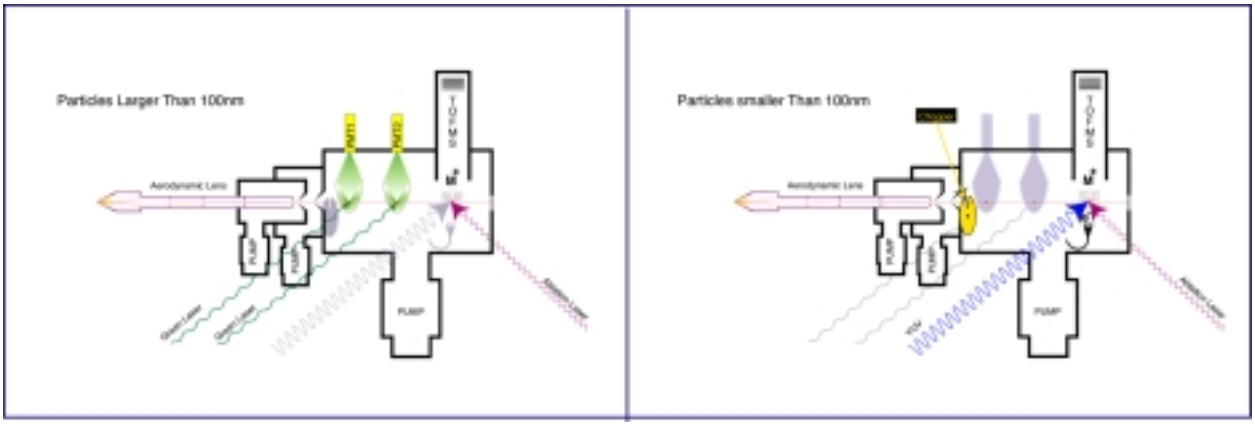



**Figure 2.** Schematic of the two modes of SPLAT-MS. Top is the optically based detection mode. Bottom shows the chopper position and the VUV ionization source.

The basic components that comprise the single particle instrument are described below.

**Aerosol inlet.** Particles and gases enter the instrument through a 100 micrometer hole at a rate of ~3 cc/sec into an aerodynamic lens system (Liu et al., 1995a; 1995b). This lens acts to focus particles in the 20 nm to 1 micrometer size range into a well defined beam of less than 1 mm diameter and very low divergence. Figure 3 represents results of fluid dynamic simulations (Jayne et al., 1999) of the trajectories of a 100 nm diameter spherical particle inside the aerodynamic lens system. Not only does the lens form a well-defined particle beam, but, as shown in Figure 4, it does so with nearly 100% efficiency. The extremely high inlet efficiency and the small particle beam are key to the instrument's high sensitivity. The lens also accelerates the individual particles to velocities that are a strong function of their aerodynamic diameter, resulting in particle velocities that are significantly lower than those produced in supersonic nozzle expansions. This fact makes it possible to aerodynamically size particles as small as 20 nm with ease. A plot of the size dependent velocity is shown in Figure 5.

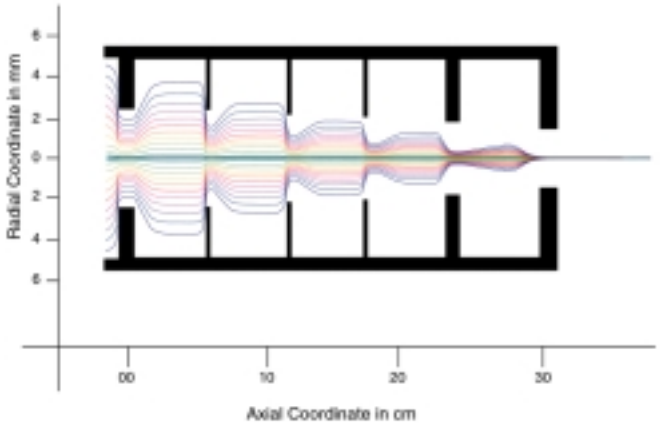



**Figure 3**. FLUENT simulation of the aerodynamic lens for 100 nm diameter spheres with density 1 g/cm$^{-3}$ at typical lens inlet pressure (2.1 torr) and volumetric flow rate (97.3 sccm). Different colored lines are the particle trajectories for particles entering at different radial coordinates. The figure also shows the physical dimensions of the lens system. (after Jayne et al., 1999).

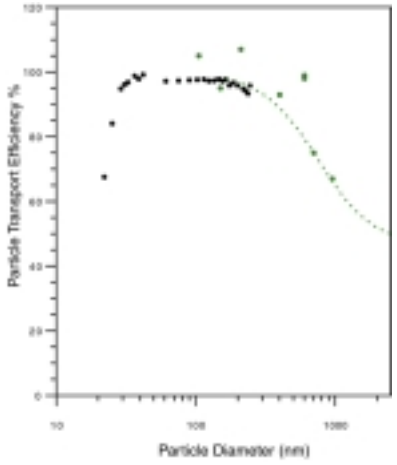



**Figure 4.** Particle transport efficiency by an aerodynamic lens system as a function of particle aerodynamic diameter (• - after Liu, 1994), (• - after Jayne et al., 1999). Note close to 100 % transmittance for particle range from 40 to 600nm.

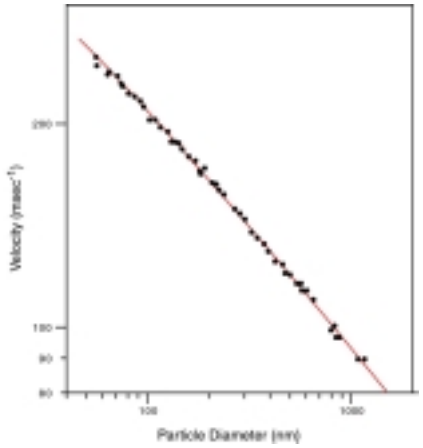



**Figure 5.** Particle velocity as a function of particle aerodynamic diameter (after Jayne et al., 1999). Such calibration curves can be used for particle sizing in the range from a few tens of nanometers to a few microns.

Avoiding significant cooling during any expansion in our inlet system prevents possible particle size and composition changes due to nucleation and growth in high-speed particle beam inlets (Mallina et al., 1997). This is particularly important for studies of small particles. Finally, it is important to note that the lens system acts to "purify" the particles relative to the surrounding gas. The particles remain in a well-confined beam, which is only ~5 times larger than the 100 micron inlet hole while the gas molecules diffuse rapidly, eventually their density drops by 11 orders of magnitude.

**Large particle optical detection and sizing.** The particle beam enters the first ellipsoidal reflector through a small hole where it intersects a green laser beam. Scatter from particles is collected by the reflector, imaged into a small pinhole and detected by a photo-multiplier. If the number of photons per microsecond (the approximate laser particle interaction time) exceeds a preset threshold, a counter is initiated. The particle beam proceeds into a second identical

reflector where the process is repeated. The time elapsed between the two signals is used to obtain the particle's time of flight between the two stages and time of flight a particle aerodynamic size is obtained. To assure high detection sensitivity, large ellipsoidal reflectors with high collection efficiency in the small angle scattering region are used to collect the scattered light. To minimize stray light baffles are used both at the entrance and at the exit of laser beam. At present the threshold is set at 3 photons/microsecond. Preliminary results suggest that this limit corresponds to ~100nm particles. The derived particle velocity is used to calculate the precise arrival time of the particle at the inlet to the TOF-MS so that a trigger signal can be generated to fire the ablation laser at the appropriate time.

**Small particle photo-ionization detection and sizing.** Light scattering by particles smaller than 100 nm cannot be distinguished from background levels of stray light in the SPLAT-MS. For smaller particles we exploit the reduction in the photoemission threshold by over 1eV of the condensed phase over that of the gas phase to generate a signal that signifies the presence of a particle. For example: the ionization potential of gas-phase water is 12.6eV while that of liquid water and ice is below 11.2eV. A continuous rare-gas resonance lamp operating with Ar and producing radiation at 11.6eV is used to photo-emit electrons from particles while leaving virtually all gas phase molecules unperturbed. The only anticipated gas phase interference is from $NO_2$ and aromatic organic molecules. However, the fact that the aerodynamic lens acts to purify the gas from the particle beam implies that the probability to ionize a 20 nm particle in 1 $cm^3$ of air is $5x10^{14}$ higher than that for the ionization of an $NO_2$ molecule in the same volume. The detection of an emitted photoelectron is used as the trigger to fire the ablation laser.

In order to determine the size of particles too small to be optically detected the aerosol beam is modulated by a chopper. Once a particle is detected, its velocity can be determined based on the time difference between detection of a photoelectron and the particle entrance through the chopper slit, using the known distance between the chopper wheel and the ionization region. The chopper will be operated at a 10% duty cycle as determined by the chopper slit size, which also defines the particle sizing precision. Note that this sizing method does not require preselection prior to analysis, therefore all particles are essentially analyzed at once. An order of magnitude estimate indicates that 0.01% of 20 nm diameter particles that enter the instrument will be detected and characterized. Larger particles can be detected with much higher efficiencies. Size measurements will be calibrated in the field using standard latex particles and differential mobility analyzer size selected ambient aerosols.

**The ablating laser.** An excimer laser is used to ablate particles and generate ions. This laser can be operated at 248 nm, 193 nm, or 157 nm. Many of the sampled ambient aerosols are expected to be composed of complex mixtures of inorganic salts and water. Because the optical absorption of these substances is very weak at wavelengths longer than 180 nm, the ablation process at 248 nm or 193 nm requires the simultaneous absorption of at least two photons by a single molecule, which is an extremely low cross-section process. In contrast, a particle containing even minute quantities of organic species, that tend to absorb at 193 nm, may ablate with probabilities up to $10^6$ higher than for a particle composed of inorganic material. To avoid a particle composition bias in our sampling, the excimer laser will be operated at 157 nm, which is a wavelength that is strongly absorbed by liquid water and all other expected aerosol constituents. Since at 157 nm the first photon is on resonance, the power density required to initiate the ablation is much lower than at the longer wavelengths, and the resulting fragmentation can be dramatically reduced. The simpler fragmentation patterns will make it much easier to identify parent molecules in the sampled particles.

**The TOF-MS.** A reflectron time of flight mass spectrometer is used for single particle composition analysis. The expected resolution of the instrument in mass-to-charge units is 2000. The TOF-MS signal are digitized and transferred at a rate of 500MHz. This rapid transfer rate

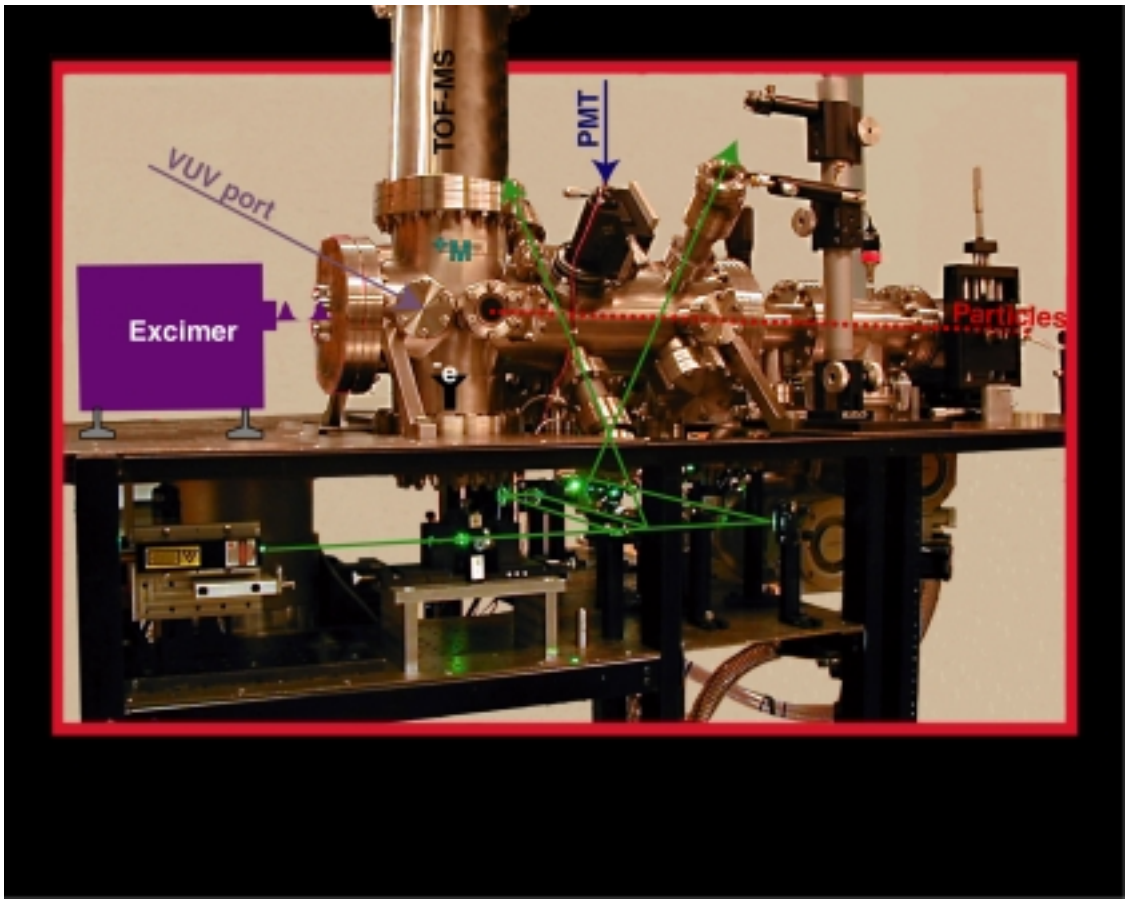



**Figure 6.** A photograph of SPLAT-MS.

allows for high-resolution mass analysis of 50 particles per second. One of the most important challenges currently facing atmospheric aerosol research is the development of methods to characterize the organic fraction of the aerosol mass. The mass spectrum of particle **a.** in Figure 1 shows that extensive fragmentation of organic compounds and low-resolution spectra yield uninterpretable spectra. By using low ablation laser power at 157 nm and high resolution mass spectroscopy we hope to be able to shed some light on the issue of organics.

**Data Analysis and Visualization** Single particle time-of-flight mass spectrometers typically characterize 1-2 particle per second, however, our SPLAT-MS system, due to high inlet transmittance, high laser frequency, and very fast data acquisition, can analyze up to 50 particle per second, generating 2-3Gb of data per day. To process this huge volume of data, some automated statistical data analysis is required. Recently the ART-2a (adaptive resonance theory) algorithm was implemented for the analysis of single-particle mass spectrometer data (Song et al., 1999). This algorithm has proved to be very useful in classifying particles into several ”major categories”. For example, one Long Beach, CA data set was divided using ART-2A into seven classes: “unreacted marine”, “reacted marine”, “organic”, “ammonium nitrate I”, “ammonium nitrate II”, “calcium”, and “soil” particles (Song et al., 1999).

We have at BNL resources in the Data Analysis and Visualization (DAV) group, lead by M. McGuigan, that are ideally suited to deal with large complex data sets and data having large numbers of variables and data sources. One example of the capabilities of the DAV group is shown in Fig. 7. DAV brings together the following advanced techniques:

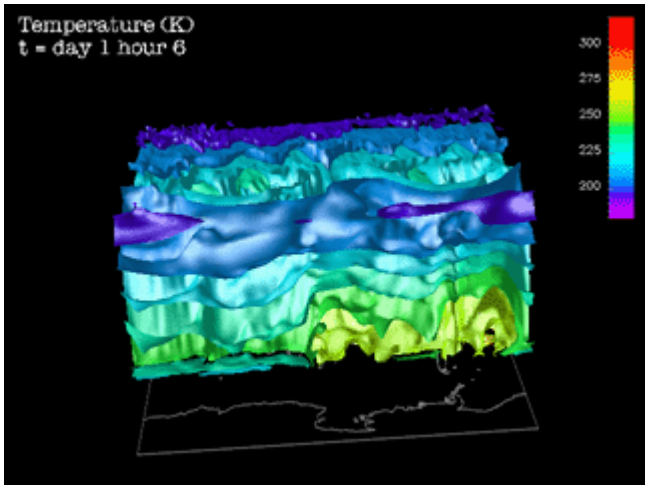



**Figure 7.** Results of a global weather simulation code used to study effects of wind and temperature on aerosol concentrations in the atmosphere. Nine isosurfaces of temperature are shown colored blue to violet to red in degrees Kelvin. Animations of the simulated temperature shows realistic features over the southern hemisphere including a temperature increase over water near Antarctica, cooling and counter rotation in the upper atmosphere.

**Data mining** algorithms discover patterns, associations and unique events in the data. It uses techniques that have existed for some time, but have only now been implemented as mature reliable tools that consistently outperform older statistical methods.

**Visualization** in 2D and 3D has also become more important in forming hypotheses about the data and in building models. The hardware and software have developed so that one can see and interact with the data in real time. Visualization has moved beyond presentation to become part of the analysis.

**Database structures** are essential to allow proper queries about the data to be asked and form a basis for more complicated analysis. Moving the raw data to a structured hierarchical database allows efficient use of advanced tools mentioned above.

A second resource unique to BNL is the Center for Data Intensive Computing (CDIC). CDIC's mission is to develop processing and analysis methods for very large volumes of data. Its challenge is to ensure that this data can be stored, retrieved, and mined for its essential information content by large geographically-dispersed collaborations. Data intensive computing challenges are common to a broad range of scientific problems throughout the DOE complex and beyond. We have been in contact with the center's director and have established a collaborative project to develop new and innovative techniques for analyzing our TOF-MS and other data. As processed data from each of our measurement systems become available, they will be submitted to the ACE-Asia data archive.

### b. Number Size Distributions from 3 nm to 50 micrometers

A combination of two measurement techniques is used to observe the aerosol size distribution over the 3 nm to 50 micron size range. Number size distributions are measured for particle diameters between 3 nanometers and 1 micrometer with a time resolution of 30 seconds using a Scanning Electrical Mobility Sizing system (SEMs, Russell et al., 1996; Endo et al., 1997), and between 0.3 and 50 microns once per second using a Particle Measurement Systems FSSP-100. Given the potential importance of super-micron dust and sea salt aerosols in the ACE-Asia region, FSSP size distribution measurements will be an important component of our overall suite of measurements.

Unlike the FSSP, the SEMs system will be located inside a measurement van and will use a sample inlet to deliver ambient particles to the instruments. A schematic of the SEMs system is shown in Figure 8. In the SEMs, different mono-dispersed particle sub-populations are

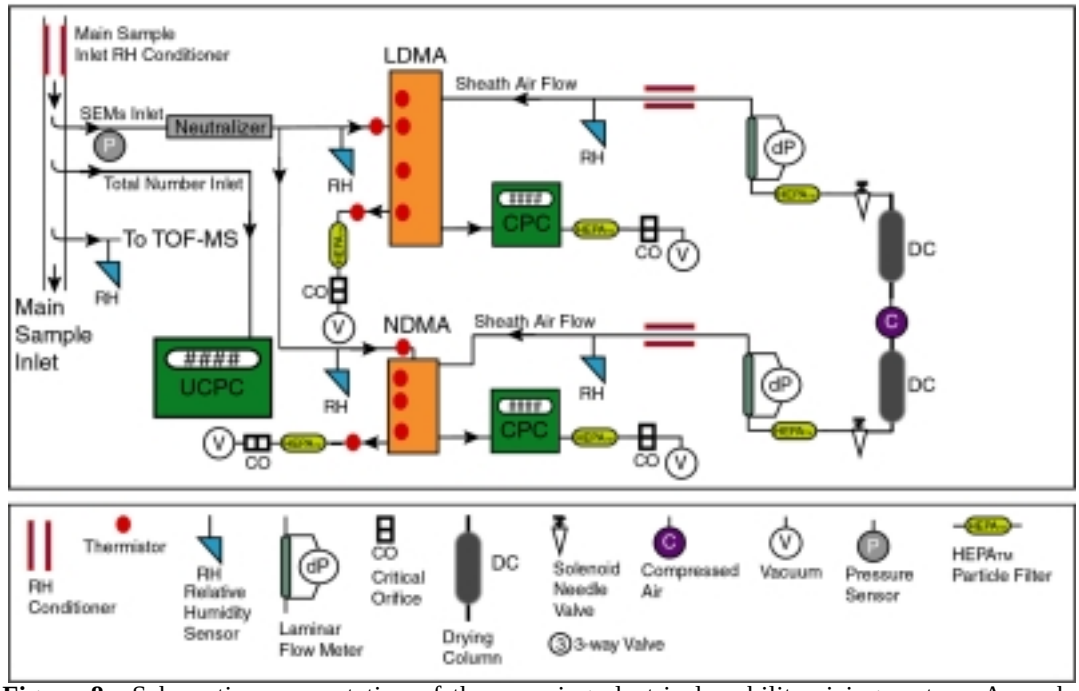



**Figure 8.** Schematic representation of the scanning electrical mobility sizing system. A weak radioactive charge neutralizer is used to impart a known distribution of charge with particle size to the sampled aerosol for the SEMs. All flows are continuously monitored and controlled by a computer data acquisition system (not shown). 'NDMA'=Nano-DMA, 'LDMA'=Long-DMA.

sequentially selected from the poly-dispersed ambient aerosol using differential mobility analyzers (DMA) and subsequently counted by condensation particle counters (CPC). The mono-dispersed sub-populations are selected using known relationships between particle size and charge, voltage, flow rates and physical dimensions in the DMA, therefore voltage and flow rate control is a critical aspect of the system design (Brechtel et al., 1998). In our SEMs system, specially manufactured high voltage power supplies and 16-bit Analog Output voltage control is used to ensure accurate voltage settings. Furthermore, flow rates are monitored and automatically controlled every 0.5 seconds to within 0.5% of their nominal setpoint values. The SEMs system can easily be reconfigured to the more traditional Differential Mobility Particle Sizing (DMPS) mode if it is necessary to improve counting statistics in the large particle size range (>200 nm).

Temperatures, relative humidities, and pressures are monitored throughout the system to ensure stable operation and to facilitate quality assurance checks of operation. SEMs, TDMA, and TOF-MS composition measurements will be performed using the same sample inlet to avoid biases in comparing the results from these different instruments. The temperature of the sample air brought into the measurement van is inevitably changed from ambient conditions, resulting in potentially large changes in sample relative humidity (RH). Changes in RH result in changes in particle size, as particles release, or take up, water. In order to remove this variability in particle size with changing RH, the sample RH will controlled 55% prior to the SEMs, TDMA and TOF-MS systems. The value of 55% is chosen to facilitate the intercomparison of our SEMs and TDMA results with similar measurements conducted on the R/V Ron Brown during the Intensive Operating Period (IOP). The automatic sample inlet RH control system will be a duplicate of the system used on the ship. The TDMA measurements are described in more detail below.

The FSSP-100 uses light scattering to determine the number size distribution of particles in the 0.3 to 50 micron range. This instrument will be mounted at a height of 10 m on a tower erected at the site for the ACE-Asia IOP. An important advantage of the FSSP probe is that particle losses due to impaction and gravitational settling inside the sample inlet are largely avoided by the instrument inlet design and deployment of the probe at ambient conditions on the

sampling tower. The FSSP measurement will be made at ambient RH and temperature, and the average ambient RH during April and May at Cheju is between 75% and 85% (Carmichael et al., 1996). Therefore, the FSSP size distribution measurements will typically be made at a higher RH than the SEMs measurement, which will be conducted at 55%. Furthermore, the FSSP measures an 'optical' diameter while the SEMs systems measures electrical mobility diameter. The relationship between these two different sizes depends in part on particle chemical composition, since the optical size depends on the particle index of refraction. At elevated RH's, the index of refraction approaches that of pure water (Nemesure et al., 1995). In the overlap region of these two systems (0.3 to 1 micron), simultaneous water uptake measurement results with the TDMA at RH's spanning the ambient RH range and TOF-MS composition measurements will be used to estimate growth factors and appropriate index of refraction values. In order to extend the TDMA technique to the 0.5 to 3 micron droplet size range, an optical probe (PCASP-100) will be employed in parallel with the second DMA of the TDMA system. The PCASP-100 is capable of measuring the size distribution of particles in 0.1 to 3μm size range. The growth and index of refraction values may then be applied to the SEMs size distribution data over the 0.3 to 1 micron size range so that closure between the FSSP and SEMs data can be evaluated. Sporadically, a second technique involving control of the operating RH of the SEMs system to the ambient RH will be employed so that FSSP and SEMs size distributions can be intercompared over the entire overlap size range between 0.3 and 1 microns.

We have substantial experience deploying particle size distribution measurement systems and interpreting observed changes in the ambient size distribution with respect to air mass source region, weather-related processes, and other factors (Brechtel et al., 1998; Kreidenweis et al., 1998; Murphy et al., 1998; Brechtel et al., 1997a; Brechtel et al., 1997b; Wiedensohler et al., 1997; Nunnermacker et al., 1998; Daum et al., 1999; Kleinman et al., 1998). A system similar to the SEMs was successfully operated over a four week period during the ACE 1 study on a remote island in the Southern Ocean (Brechtel et al., 1998; Kreidenweis et al., 1998). The current SEMs system was successfully deployed on-board a research aircraft in a 1999 U.S. EPA-sponsored "Special Opportunities" program in Philadelphia (Brechtel, 1999a; Brechtel, 1999b), and will also be used in the Texas-2000 study in Houston. The single particle mass spectrometer is scheduled for field deployment during Texas-2000, and in New York city during the summer of 2001 and the spring of 2003 during the New York EPA Super-Site experiments.

### c. Particle Hygroscopicity, Volatility and Surface Properties

Condensation, coagulation and chemical reactions are examples of important processes that influence particle size and chemical composition as the aerosol is transported through the atmosphere. On the other hand, the extent to which these processes can alter the physical and chemical characteristics of particles depends to some degree on the particle properties themselves. The morphology, size, composition and concentration of pre-existing 'primary' particles within a given air mass often determine the processes that are capable of exerting control over aerosol properties. For example, near industrial sources of condensible vapors and very small particles, coagulation and condensation can significantly alter the composition of pre-existing dust particles from outside the region. However, if the surface area of pre-existing particles is sufficiently small, substantial new particle formation through gas-to-particle conversion may be preferred to condensation on the pre-existing particles. Given the non-linear relationships between particle size, composition and, for example, hygroscopic growth, techniques are required that can reveal how particles of different sizes and composition respond to changes in thermodynamic conditions that mimic atmospheric processes.

Using tandem differential mobility analysis techniques (TDMA, Brechtel and Kreidenweis, 2000a; Brechtel and Kreidenweis, 2000b), we can perform on-line sampling of monodisperse particles from the polydisperse ambient particle size distribution at a controlled RH, condition the monodisperse particles in various ways, and determine the size change of the conditioned

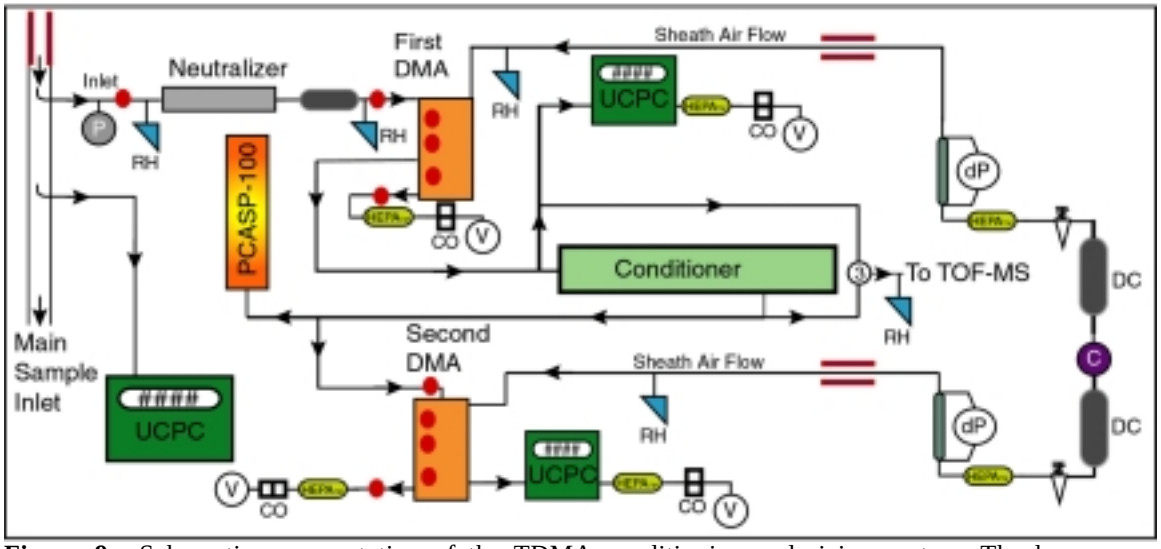



**Figure 9.** Schematic representation of the TDMA conditioning and sizing system. The lower case conditioner may be used to examine size-resolved volatility, hygroscopicity or photoelectric charging properties. Symbols and acronyms are described in Figure 8.

particles using a second DMA or optical scattering spectrometer probe (PCASP-100) sampling after conditioning (see Fig. 9). Several 'intensive' TDMA experiments will be conducted during the IOP, when the TOF-MS system will be configured to sample particles both immediately before and after the conditioner. These simultaneous TDMA/TOF-MS measurements will be the first time TOF-MS measurements of particle composition will be coupled with the TDMA technique so that composition, size, and number concentration changes due to controlled conditioning can be observed simultaneously.

During ACE-Asia, three different properties of the ambient samples will be investigated during several individual intensive experiments lasting several hours: hygroscopic growth via RH conditioning, volatility via controlled thermal desorption, and surface absorbates via *in situ* aerosol photoemission. The 'continuous' operating configuration of the TDMA system will be in the hygroscopic-growth measurement mode, with the first DMA RH set to 55% and the conditioner, second DMA, and PCASP-100 RH's controlled to 10%, 40%, 55%, 70%, 80%, 90% and the ambient RH observed during the sampling period. The particle/droplet sizes measured by the second DMA and PCASP-100 at controlled values of RH will provide critical information for the validation of models and remote sensing algorithms that attempt to close the radiation budget in the atmospheric column over Cheju. Approximately five different monodisperse particle sizes will be sequentially selected by the first DMA to give measurement results representative of the sea-salt/dust (250-1000 nm), accumulation (100-250 nm diameter), and Aitken (30-50 nm) modes, as these modes are expected to dominate the total ambient mass and number concentrations. The above relative humidities and initial DMA particle sizes have been chosen to match those that will be used on-board the R/V Ron Brown so that the measurements at Cheju Island can be easily compared with those on the ship.

One strength of the TDMA/conditioning technique is that it is sensitive enough to detect monolayer changes due to evaporation or condensation (Rader and McMurry, 1986). For example, controlled thermal desorption of water, sulfates, nitrates and organic compounds from monodisperse ambient particles at different temperatures will be studied by heating the monodisperse aerosol in the conditioner. By monitoring changes in particle size with the DMA after the conditioner, the number concentrations of internally mixed particles at a given size can be determined. Analysis of individual particle chemical composition using the TOF-MS system will reveal the chemical species responsible for the observed size change and allow an unambiguous

connection to be drawn between changes in hygroscopic, volatile or surface charging response measured by the TDMA and chemical composition observed using TOF-MS.

Another conditioning technique that will be employed in the TDMA to probe the surface properties of particles is photoelectric emission (Burtscher et al., 1993). Here, the monodisperse particles exiting the first DMA are exposed to radiation from a Hg lamp ($\lambda$= 254 or 187 nm) in the conditioner to induce photoelectric charging on the particles. The photoemission characteristics of a particle surface depend upon the surface bulk composition, and on the composition of any adsorbed materials, for example, polycyclic aromatic hydrocarbons (PAHs), other volatile organics, or other materials. The first DMA selects singly, negatively charged particles in the size range of interest, and the emission of one electron, stimulated by irradiation of the particles in the conditioner, will charge neutralize the particles. The emission of two or more electrons from a particle will result in a net positive charge on the particle. The second DMA sizes particles according their accumulated number of charges, and the monodisperse particles exiting the conditioner will be either negatively charged (unaffected by the conditioner), charge neutral, or positively charged. Therefore, the voltage of the second DMA will be scanned using both negative and positive voltages to determine the number fractions of particles with different photoelectric yields. The sizing technique of the PCASP-100 is not sensitive to particle charge, therefore, it will not be used during these studies. Siegmann and Siegmann (1997) have shown that photoemission is a valuable tool for the study of soot particles and organic coatings. The presence of different surface compounds will be simultaneously investigated using single-particle TOF-MS measurements made before and after the conditioner in the TDMA.

### d. Ex-Situ Microscopic and Chemical Single Particle Analysis

Ex-situ sampling is carried out in collaboration with James Cowin from Pacific Northwest National Laboratory (PNNL). Ex-Situ SEM automated particle analysis and elemental analysis has been pioneered by Buseck and De Bock (Katrinak et al., 1995; De Bock et al., 1994). At PNNL innovative techniques that combine automated sampling and analysis have been developed to meet the high time resolution requirements for field aerosol composition analysis using a small, inexpensive automated sampler to archive 1000's of samples. A photo of the sampler is shown in Fig. 10. The samples are analyzed in the lab on a single particle basis by fully automated scanning electron microscopy/energy dispersed x-ray analysis of x-rays (SEM/EDAX), and on an as-needed basis by very high resolution time-of flight secondary ion mass spectrometry (TOFSIMS). Samples can be obtained as often as once per minute. Automated single particle SEM/EDAX sizes and chemically classifies thousands of particles per lab-day, from 0.1 micron and up, identifying soot, minerals, sea salt particles, and trace constituents at 1% levels. TOFSIMS (not currently automated) will examine critical samples to identify organic species, inorganic compounds, and to depth-profile individual particles to probe their history. Other single particle techniques available at PNNL are scanning auger electron spectroscopy, ideal for depth-profiling elemental composition, and an "environmental" scanning electron microscope to observe the hygroscopic nature of individual particles from 0 to 100% relative humidity.

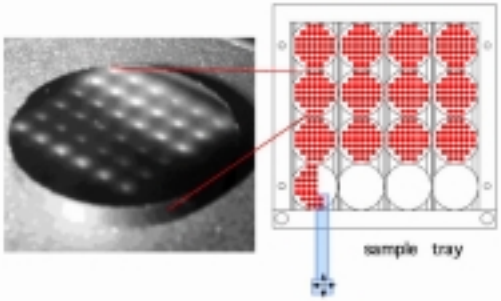
The PNNL field collector samples will also be used at BNL for analysis at the National Synchrotron Light Source (NSLS). The X1-A beam line at the NSLS is equipped with an atmospheric pressure X-ray microscope. Images of single particles can be obtained with a resolution of ~5 nm at any RH. This set up will make it possible to observe the changes in particle shape as a function of RH. X-ray fluorescence can then be used for elemental analysis.

# Instrument Capabilities

Fully-Automated Time-Resolved Field Collector
Lab-Based Single-Particle Analysis

## Collector (current configuration)

time per sample: 1 minute minimum
# samples : 1600 samples
duration of monitoring = 1 to 100 days
=1600* (time per sample)
dimensions: 30 cm X 30 cm X 30 cm
power: 110 VAC at 200 W




## Collector (redesigned)

# samples : 1600 samples
duration of monitoring = 1 to 100 days
=1600* (time per sample)
dimensions: 15 cm X 15 cm X 8 cm
power: solar powered with battery

## Analysis

- LEO 982 field emission scanning electron microscope, with Energy-Dispersed Analysis of X-rays (EDAX)
- Oxford Instruments software for fully automated particle analysis

> 2000 particles per day analyzed, typed.

- Identification of particle compositions versus time (silica, clay, hydrocarbon, feldspar, asbestos fiber, etc)
- Monitor toxic trace elements at 0.1% level (As, Pb, Cd, ...)
- Identify "rare" particles, example: pure lead or $UO_2$ particles
- Above ideal for identifying particle sources and assessing hazards.

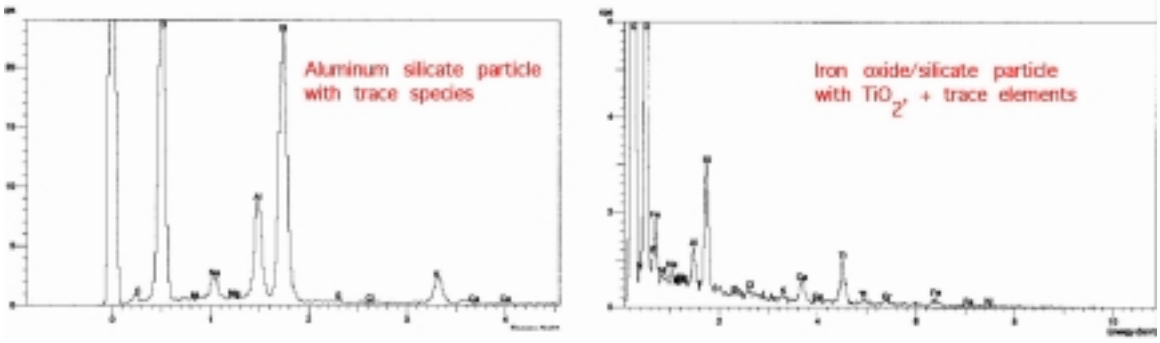



**Figure 10**

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